

Molecular and Electronic Structure of PTCDI and Melamine-PTCDI Complex

V. Chiş, R. Ştiufluic, N. Leopold

Babeş-Bolyai University, Faculty of Physics, Kogalniceanu 1, RO-400084, Cluj-Napoca, Romania

Perylene derivatives received great scientific interest in the last years due to their potential applications in molecular electronics. Particularly, 3,4,9,10-perylene-tetracarboxylic diimide (PTCDI) and the anhydride analogue (PTCDA) were the subject of studies aiming to elucidate their absorption mechanism on different substrates [1]. Recent studies are reported on the hydrogen-bonding guided assembling by co-adsorption of PTCDI and melamine (1,3,5-triazine-2,4,6-triamine) on silver terminated silicon [2] or gold surfaces [3].

In this work we will report on the molecular and electronic structure of PTCDI, melamine and melamine-3PTCDI complex (Fig.1). The complex is stabilized by strong intermolecular hydrogen bonds whose calculated lengths at B3LYP/6-31G level of theory are 2.914 Å and 2.888Å for NH...O and N...HN bonds, respectively. The calculated center-to-center spacing of PTCDI-melamine (9.972 Å) pair is in excellent agreement with the observed separation of 9.98Å [2].

Infrared and Raman spectra of PTCDI and melamine-3PTCDI complex were calculated and the experimentally observed spectra were safely assigned based on theoretical data. Important shifts are observed for the imide groups whose $\nu(\text{NH})$ wavenumbers are 3583cm^{-1} in free PTCDI and 2790cm^{-1} in melamine-3PTCDI complex.

Molecular orbitals energies of the PTCDI molecule are calculated at different levels of theory, using DFT methods. The influence of an external electrostatic field on the shape and energies of the frontier orbitals and HOMO-LUMO gap is investigated. The field shifts both the HOMO and LUMO energy levels and their spatial distribution. The gap decreases drastically by increasing the strength of the applied external field parallel to the molecular plane and it remains almost insensitive when the external field is applied perpendicular to the molecular plane.

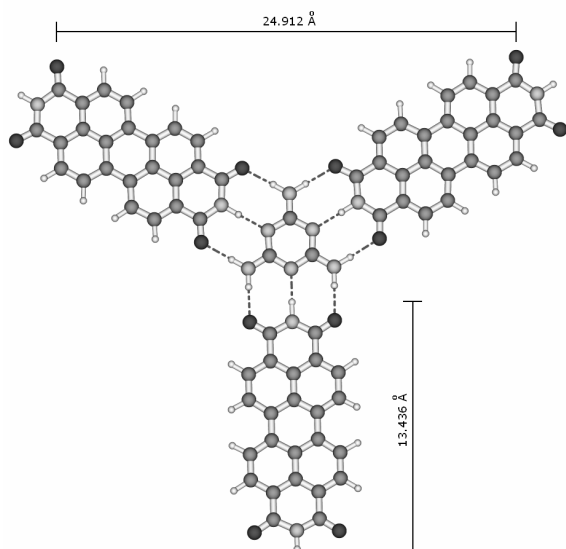


Fig. 1: B3LYP/6-31G optimized geometry of the melamine-3PTCDI molecular complex

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